On the Osmotic Pressures of Aqueous Solutions of Calcium Ferrocyanide. Part I.—*Concentrated Solutions.*

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(Abstract.)

The principal aim of this paper was to test the nearness of possible approach to complete osmotic efficiency for strong solutions. To this end the experimental verification of the exact physical equation given by A. W. Porter* was undertaken, a membrane having been constructed which could withstand osmotic pressures of calcium ferrocyanide up to 150 atmospheres without any sensible percolation of the solution. It was found, notwithstanding many precautions, that the formula would not verify within about 3 per cent. But further consideration showed that this formula must refer to osmotic pressures *in vacuo*, whereas the experiments were necessarily conducted in air at atmospheric pressure. Reconstructing the argument in terms of ideal osmotic partitions impermeable to air but permeable to the solution, the equation was modified so as to apply strictly to the quantities involved in the experimental determinations, which required the addition of the atmospheric pressure to the limits in the first and third of the integrals concerned in it.

The final results are given in the following table:—

I. Weight concentration.	II. "Unmodified" equation.	III. "Modified" equation.	IV. Observed equilibrium pr.
49·966	135·04 atmos.	131·45 atmos.	130·66 atmos.
47·219	116·05 „	112·96 „	112·84 „
42·889	88·99 „	86·61 „	87·09 „
39·503	72·54 „	70·61 „	70·84 „
31·388	42·38 „	41·24 „	41·22 „

From the concordance of these numbers, it may fairly be deduced that the membrane establishes, unambiguously, even with concentrated solutions, the full theoretical osmotic pressures, for the thermodynamic relations, at these high pressures, are completely verified.

* 'Roy. Soc. Proc.,' A, vol. 79, 1907, p. 519.